



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB91/01244 <b>(22) International Filing Date:</b> 25 July 1991 (25.07.91)  <b>(30) Priority data:</b> 9016340.3                      25 July 1990 (25.07.90)                      GB  <b>(71) Applicant (for all designated States except US):</b> DEVRO LIMITED [GB/GB]; Moodiesburn, Chryston, Glasgow G69 0JE (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> TANNER, Alistair, Gilmour [GB/GB]; 10 Dougalston Crescent, Milngavie, Glasgow G62 6HP (GB). HARVEY, Wilson [GB/GB]; 23 The Glebe, Gargunnoch, Stirling FK8 3AX (GB).		<b>(74) Agent:</b> FISHER, Adrian, John; Carpmaels & Ransford, 43 Bloomsbury Square, London WC1A 2RA (GB).  <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN + (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MOISTURE BARRIER FILM  <b>(57) Abstract</b>  A moisture barrier film, which is of particular utility in the manufacture of food products, comprises an edible protein and an edible polysaccharide. The film is rendered at least partly moisture-impermeable by the provision of a coating of an edible hydrophobic material on at least a portion of a surface thereof.		

# + DESIGNATIONS OF "SU"

It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

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MOISTURE BARRIER FILM

This invention relates to a moisture barrier film, and more particularly to an edible film which is suitable for use as a moisture barrier in food products.

Films have been used in food preparations for various reasons for centuries. These applications include the protection of raw and cooked foods, the containment of wet foods and flavours, the separation of wet from dry foods, and the preventing of drying. Examples of the use of natural films in food products are sheep/hog stomach for wrapping comminuted meat as in haggis, and the use of intestines for the manufacture of sausages (see Tannahill, R., "Food in History", pub. Stein & Day, NY.). In this century, the evolution of plastics films and plastics laminates has allowed a great diversification in food wrapping for the purposes of protection from gross and microbial contamination, inhibition of oxidation, and containment (see Daniels J.A. et al (1985) J. Food Protect. 48, 532; Neilsen, H.J.S. (1983) J. Food Protect. 46, 693; and Jantavat, R. & Dawson, L.E. (1980) Poultry Sci. 59, 1053).

Collagen, a naturally occurring connective tissue protein, has been used for the manufacture of food wrapping films on a commercial basis. Films of this type are disclosed, for example, in US-A-3664844 and US-A-3529530. The benefits of using collagen for the manufacture of food films are that it is a natural product, the chemistry of which is well understood (see Ramachandran, G.N. & Reddi, A.H. (eds.) (1976) "Biochemistry of Collagen", pub. Plenum Press, NY. & London), it can be readily comminuted and converted to a viscous gel or mass and it can be extruded in a number of forms including films (see Chvapil, M. (1979) in "Fibrous Proteins: Scientific, Industrial and Medical Aspects", Vol. 1, pp. 247 et seq (D. Parry & L. Creamer, eds.), pub. Academic Press, NY. & London). Collagen films

are also machinable (in the sense that they can readily be reeled, cut and handled by machinery), and they may be used in the preparation of heat-sealed pouches.

5 International Patent Application No. WO-A-8802991 discloses an alternative film derived from soya protein, casein, albumin or gelatine with polysaccharides such as gum arabic and starch. Such a film, like conventional collagen films, is moisture-permeable.

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Moisture-impermeable films have also been widely used in the food industry. These include, for example, the plastics food wrappings already mentioned above. Much earlier examples include the use by the ancient Chinese of  
15 edible wax coatings on fruit to prevent drying during storage and the use of fat wrappings (lardings) in 16th century Britain.

More recently, a non-edible, disposable food wrap made  
20 from a laminate of saccharides and vinylon film has become available from Showa Denko K.K. of Japan. This film is said to absorb moisture, thereby limiting moisture migration.

Japanese Patent No. 301387 (Kanebo K.K.) describes a  
25 zeolite-based non-edible film with moisture absorbing ability which is claimed to extend shelf-life.

Some attempts have also been made in recent years to produce commercially viable films which are both edible and  
30 moisture-impermeable. For example, wax and protein sprays have been used in the bakery industry, but with little success.

The combination of fatty acids and modified cellulose  
35 with wax layers has been reported for use as a moisture barrier film (see Kamper, S.L. & Fennema, O. (1984) J. Food Sci. 49, 1478 and 1482; and (1985) J. Food Sci. 50, 382; Kester, J.J. & Fennema, O. (1989) J. Food Sci. 54, 1383 and

1390; and Greener, I.K. & Fennema, O. (1989) J. Food Sci. 54, 1393 and 1400). However, such cellulose-based films have low strength and poor handling characteristics.

5 EP-A-0269460 describes a collagen film coated with a fine layer of emulsified animal fat as a wrap for meat products which prevents moisture loss. This product is a combination of the film wrap and larding techniques and is only applicable to meat "logs" or round joints.

10

According to the present invention, there is provided a film comprising an edible protein and an edible polysaccharide, said film having a coating of an edible hydrophobic material on at least a portion of a surface  
15 thereof.

The invention thus provides an edible film which is at least partially moisture-impermeable. Preferably, the film is coated with the hydrophobic material over substantially  
20 the whole (for example, greater than 95%) of at least one surface, such that the film is substantially completely moisture-impermeable. By way of example, the film may have a moisture permeability of less than  $5\text{g/m}^2/\text{day/mm Hg}$ , and more preferably less than  $2\text{g/m}^2/\text{day/mm Hg}$ . If desired, the  
25 film may be coated with the same or different hydrophobic materials on the two major surfaces thereof.

The moisture permeability of the films of the invention may be measured by maintaining a difference in water vapour  
30 pressure across the film, and then measuring the mass of water which passes across the film per unit area. A suitable technique (and the one used herein) is that described by Kester & Fennema, (1989) J. Food Sci. 54, p.1384, modified in that water vapour pressure in the  
35 container is maintained at zero by means of anhydrous silica gel, rather than anhydrous calcium chloride. The film is sealed over 100ml glass jars each containing approximately 20g of preweighed silica gel, and exposed to a saturated

atmosphere of water vapour in air in a desiccator at 20 °C. The rate of water vapour transmission through the film is calculated from the weight gain in the silica gel after 48 hrs exposure.

5

The edible, moisture-impermeable films of the invention are of value in a variety of applications in the food industry. One such application is in the manufacture of foods which contain both wet and dry domains. Examples of such foods include most bakery, pie-type products (such as quiche lorraine, meat pies, fruit pies and pasties), and also pizzas. A quiche filling may typically have a water activity (Aw) of 0.97 - 0.99, while the pastry base may have a water activity of 0.92 to 0.98. In such products it is common in industry for the filling and pastry to be cooked together in the final product. Such products, therefore, have wet and dry domains in close contact and this can cause problems on storage. Moisture from the wet domain can easily migrate into the dry domain (the pastry), thus wetting it and making it more susceptible to microbial spoilage and at the same time making it organoleptically less acceptable. Such reactions cause a lowering of the viable shelf-life of pies and related products, so that, for example, some superior products of this type may have a chilled shelf-life of only 24 hours. The film of the present invention, providing as it does an effective barrier between the wet and dry domains of mixed food products, considerably enhances the shelf-life of such products.

30 The protein component of the film of the invention is important because it helps to maintain the integrity of the film during cooking, so that the moisture-barrier properties are retained even after cooking. This is in contrast to the fatty acid/modified cellulose films of the prior art, which are dissipated on cooking, and which are therefore useful as moisture barriers only for uncooked products. Moreover, the films of the invention are extrudable, and have better handling properties (including increased tensile strength

and tear strength) in comparison to such prior art films.

Surprisingly, the films of the invention are generally undetectable (whether visually or organoleptically) in the cooked products. Moreover, the films of the invention are of low cost and are readily handled by machinery.

Other applications of the films of the invention include the formation of pouches which can be used for portion control in the manufacture of pies and similar food products. Of particular advantage in this application is that the films may be heat-sealable.

The edible protein which is used in the film of the invention is preferably insoluble and fibrous, but globular proteins such as casein, albumen and blood proteins may also be used. Examples of suitable fibrous proteins are collagen, keratin and elastin, of which collagen is preferred. The protein may be used in its natural form, or it may be physically or chemically modified prior to use. For example, the fibre length of a fibrous protein may be reduced to less than 0.1mm by physical means such as by forming a fibre gel and then homogenising the gel.

Chemical modification of the protein may include (a) solubilisation by proteolysis (using, for example, pepsin), (b) cross-linking by agents such as aldehydes (e.g. glutaraldehyde or reducing sugars), and aluminium salts, (c) denaturation by heating to induce partial or complete gelatinisation, and (d) hydrolysis with acid or alkali. Two or more such chemical modifications may be used in combination. For example, collagen may be hydrolysed with acid or alkali to form gelatin, and subsequently cross-linked to reduce its solubility during cooking.

When collagen is used as the edible protein, it may suitably be obtained from limed bovine corium, i.e. the inner layer of the skin of male or female cattle, which has

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been dehaired and limed using standard commercial procedures. The material may be supplied as whole hide-sized pieces, or may be substituted by any other bovine corium material from any part of the whole hide, e.g. belly  
5 "splits", hide off-cuts. Other hide materials can be substituted for this raw material including the hides of any of the domestic meat animals, e.g. pig, sheep, deer, goat, chicken, turkey and other species commonly used for food in various parts of the world e.g. the skin of fish or  
10 kangaroo.

The polysaccharide is preferably film-forming and soluble. Examples include charged polysaccharides (e.g. pectin, alginates, agars, carageenans, and chitosan), gums  
15 (e.g. arabic, acacia, tragacanth, locust bean and guar), and modified celluloses (e.g. cellulose ethers such as methylcellulose, ethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose, hydroxypropylethylcellulose and carboxymethylcellulose).  
20 Starches such as corn flour, crystal gum<sup>TM</sup>, Dry-Flow<sup>TM</sup>, and National Starch B38<sup>TM</sup> may alternatively be used. The preferred polysaccharide is hydroxypropylmethylcellulose (HPMC).

25 The hydrophobic material should preferably be tasteless, odourless, solid at room temperatures, and pliable, resisting cracking and flaking when the coated film is manipulated. Suitable hydrophobic materials include edible oils and waxes, such as coconut oil, palm oil, palm kernel  
30 oil, acetylated monoglyceride (Dynacet), glycerol monostearate, calcium and sodium steroyl lactate, polyglycerol ester and beeswax. Acetylated monoglyceride is preferred.

35 The film will generally contain protein in an amount of from 5 to 75%, more preferably from 15 to 35%, and most preferably from 20 to 30% by weight of protein plus polysaccharide. The film may additionally contain



plasticisers, flavourings, colourings and preservatives. The protein content of the uncoated film, including plasticisers and other components, will usually be from 3.5 to 60% by weight, more usually from 12 to 25% by weight, and 5 most preferably from 15 to 22.5% by weight.

Suitable plasticisers include glycerol, sorbitol and polyethylene glycol, in amounts up to 40% by weight of the uncoated film. Preferably, the film contains plasticiser in 10 an amount of from 5 to 30% (and more preferably from 20 to 30%) by weight of the uncoated film.

Flavourings for the film include artificial and naturally occurring flavours, spices and herbs. Suitable 15 colourings include caramel and other permitted artificial or natural food dyes, and are generally employed in amounts less than 5% by weight of the uncoated film. Preservatives, such as propionic acid, sorbic acid, sodium nitrate and sodium nitrite, will usually constitute less than 1% by 20 weight of the uncoated film.

The film may be formed by extrusion from a collagen/polysaccharide gel. The gel preferably has a solids content in the range 2 to 10%, and more preferably in 25 the range 4 to 7%. After extrusion, the gel film is dried by any suitable means, such as by hot air. Preferably, the film is then brought up to a pH of from 6 to 8 by passage through an atmosphere of ammonia.

30 The hydrophobic material will generally be applied to the film in an amount of from 10 to 50 g/m<sup>2</sup>, and more preferably from 20 to 40 g/m<sup>2</sup> of film surface, to produce a coating which is from 10 to 50 micrometers thick. Suitable coating techniques include dipping and brushing, but it is 35 preferred to apply the coating by means of a heated roller or spray.

The films of the invention, and methods for their

manufacture, are now further illustrated by reference to the following example, and to the Figures, in which:

Figure 1 is a graph showing the results of penetrometer studies of the pastry base of a quiche prepared with the film of the present invention, and

Figure 2 is a graph showing the effect of the film of the invention on the moisture content of quiche pastry.

10

#### EXAMPLE

##### 1. Washing and decalcification of hides

15 Limed bovine corium (or other suitable collagen source) is placed in a large rotating vessel, e.g. a stainless steel Challenge-Cooke mixer or any other similar devices for freely mixing the raw material with water and other solvents to aid rapid washing/decalcification. Several deliming agents which remove chemically deposited and chemically bound lime by conversion into readily soluble salts can be utilized, e.g. ammonium sulphate, CO<sub>2</sub> deliming systems, hydrochloric acid, malic acid, acetic acid, lactic acid, citric acid-sodium citrate, or ammonium chloride.

25

The temperature of the system should be less than 20°C. The procedure is continued until the final liquor pH is approximately 4.5 - 5. The hides are then washed in water and drained. The washed hides may then be stored at 2 -10°C or deep frozen until required. The temperature of all solvents at all stages should be less than 20°C.

30

##### 2. Grinding

35 The washed, decalcified and salted raw material is passed through a grinder for initial comminution. The whole pieces of corium are fed continuously into a grinding device such as a Weiler or Wolfking industrial food grinder. The

material is passed through a plate or plates with 5mm-10mm holes such that 100% of the material is comminuted into approximately 5mm-10mm sized pieces of wet grind. The temperature of the material should be minimised at this stage. This wet grind is then transferred immediately to the next stage.

### 3. Comminution and mixing

The grind is pumped with water directly from the Wolfking or Weiler grinder to a hide and water holding tank. The resulting slurry is further comminuted by passing through Karl Schnell Mincemasters using plate sizes in the range of 1-5mm or through a Stephan Microcut. The temperature rise is minimised at this stage and the resultant collagen pulp stored in the pulp holding tank. Food grade hydrochloric acid, glycerol, sorbitol and optionally aluminium sulphate are then charged to a second holding tank (Acid Tank), together with water and ice. Suitable final concentrations in solution of these components are within indicated ranges:

	hydrochloric acid	.075 - 1.0%
	glycerol	.5 - 1.0%
25	sorbitol	4 - 6%
	aluminium sulphate	.005 - .01%

The contents of the pulp tank and acid tank are blended together using a Stephan Microcut or similar high shear mixer or a Nauta mixer. The desired gel constituents are obtained and the resultant gel is stored in a blend tank for a minimum of 12 hours.

### 4. Preparation of collagen/polysaccharide gel

The collagen gel thus obtained from the previous step is mixed in a Giusti pressure/mixing vessel, using iced water for cooling, with a solution of polysaccharide

containing sufficient plasticiser to give a final solids content of 3.5% with a ratio of 25:75 collagen:polysaccharide by weight and the same final percentage of plasticiser as in the collagen only gel.

5 Suitable polysaccharides include guar gum, locust bean gum, National Starch B38, crystal gum, "Dry-Flow", corn flour, methyl cellulose and hydroxypropyl methyl cellulose (HPMC), preferably HPMC.

10 The resulting gel is homogenised using a Cherry Burrell homogeniser with automatic pressure control ( $34.5 \pm 1.4$  MPa, ie  $5000 \pm 200$ psi, with a minimal temperature rise) and passed into a line tank at a minimum of -730mm Hg via a deaerating distributor. The tank is pressurised to 270 kPa  
15 (2.7 Bar) and the gel then passed through two gel filters. Four filter banks are used to allow changing of gel filters - 2 for the first filter (placed in parallel) and 2 for the second filter (placed in parallel). The first and second filters should be placed in series, and the gel filters  
20 should be capable of retaining particles greater than 0.076mm (0.003").

#### 5. Extrusion

25 The gel is transferred directly to an extruder. For extrusion, the gel is maintained at a maximum temperature of  $19 \pm 4^\circ\text{C}$  and extruded at 345 kPa (50 psi) onto a suitable conveyor, such as a PTFE (polytetrafluorethylene) coated glass fibre belt. The film is then batch-dried on the  
30 conveyor at  $45^\circ\text{C}$  for approximately 20 mins.

#### 6. Hydrophobic coating

35 A hydrophobic layer is applied to one surface of the film using a heated roller loaded with the coating material, producing an even coating approximately 12.5 micrometres (0.0005") thick. Materials tested were: coconut oil, beeswax, palm oil, palm kernel oil, acetylated monoglyceride

(Dynacet), glycerol monostearate, calcium and sodium steroyl lactate and polyglycerol ester.

## 7. Cooking Trials

5

### (i) Quiches

Quiches were prepared in 200 mm or 140 mm diameter aluminium moulds

10

Pastry ingredients:	% w/w
Flour, soft plain white	58.7
Margarine	29.3
15 Water, chilled	11.7
Salt	0.3

Half the flour and all the margarine was blended in a food processor to form a smooth paste. The salt was  
20 dissolved in the water and creamed into the mixture. The other half of the flour was added and the mixture processed to a homogeneous ball of pastry. 250g or 120g of pastry was rolled by hand to 4mm thick and pressed into the mould and trimmed. The base of the pastry was pricked to prevent  
25 expansion of air bubbles distorting the pastry during cooking.

Filling ingredients:	% w/w
30 Milk, skimmed	74.8
Eggs, whole	24.9
Salt	0.3

The milk was heated to 50°C and the eggs and salt beaten  
35 in. 330g or 200g (for smaller quiches) of filling was added to the raw pastry base. In the experimental quiches, the pastry base was first covered with the film of the invention, with the hydrophobic surface uppermost. The

quiches were cooked in a preheated oven (190°C) for 25 minutes, then the temperature reduced to 150°C for a further 15 minutes. The quiches were then removed, allowed to stand for 5 minutes, loosely covered with foil then chilled to 2°C in less than 90 minutes.

(ii) Meat Pies

Pastry was made to the recipe described above, and 1400mm diameter aluminium moulds were lined with 4mm thick rolled pastry. 200g of commercial tinned meat filling in gravy was added directly to the pastry shell or retained within an experimental film pouch prior to placing in the shell. A top crust (80g of pastry) was placed on top of the pie. Pies were baked at 175°C for 35-40 minutes, allowed to cool to room temperature, then chilled to 5°C.

8. Assessments

(i) Shrinkage

Any shrinkage of the film was detected visually on separation of the filling from the pastry base.

(ii) Penetrometer Studies

A characteristic of the pastry base which varies with moisture content is the resistance to deformation under applied pressure. This was measured in 50mm discs cut out of the pastry after removal of the filling, using a Lloyd tensile tester, type 5002, with an 8mm diameter probe attached to a 100 Newton load cell, crosshead speed 25mm per min. The characteristic of the stress/strain curve which was used was the peak height (Fig. 1), corresponding to "firmness" or resistance to penetration; this was expressed as Newtons (N).

(iii) Moisture Content

The filling was separated from the pastry base and both  
5 were ground to homogeneity. 10g samples were weighed before  
and after heating at 80°C to constant weight (6h for pastry,  
20h for filling). 5 replicate samples were taken from each  
pie or quiche.

10 (iv) Sensory Assessment

A standard triangle taste for sensory difference was  
used with a randomly selected panel of 24 tasters. Samples  
of quiches were allocated random codes and the mode of  
15 presentation was balanced. Identification of one film-  
containing sample from two control samples was evaluated  
using the BS 5929, Part 1 (1980) test.

20 9. Results

(i) Film Production

No problems were encountered with the production of  
collagen/polysaccharide films; all those produced had  
25 sufficient mechanical strength and flexibility for handling.

(ii) Heat-sealing of Film

It was found possible to seal portions of pre-filling  
30 into film pouches, using a heated metal bar, prior to  
placing in the pie case.

(iii) Shrinkage on Cooking

35 Collagen film with no polysaccharide component shrank  
during cooking in quiches, exposing the pastry base and  
allowing penetration of moisture from the filling. However,  
inclusion of polysaccharide in the collagen film

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substantially reduced this thermal shrinkage: Methocel showed no detectable shrinkage during cooking in quiches.

(iv) Water Migration in Quiches

5

Examination of the pastry base typically showed three layers:

- 10           1.       Closest to the filling was an opaque, white, soft, greasy layer.
2.       A central layer which was white, dry and "crumbly" with small visible air spaces.
- 15           3.       An outer layer, in contact with the cooking container, which was pale brown, dry and crumbly.

(a) Moisture Content

20       The migration of moisture from filling into the pastry base increased with time, illustrated by the change in water activity (Table 1). This change was confirmed by measurement of moisture content (Figure 2, upper curve).

25       Incorporation of the film of the invention into quiches significantly reduced the rate of moisture migration into the pastry, determined by moisture content. The results of comparative tests involving the use of films coated with different hydrophobic materials are set out in Table 2. The  
30 best results were obtained with acetylated monoglyceride as the hydrophobic material. Not only was this most effective in reducing water migration, but it also had the best characteristics for application, adherence, flexibility, taste and mouthfeel, and it was therefore used for all  
35 subsequent tests.

A further series of comparative tests showed that a film comprising hydroxypropylmethylcellulose as the

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polysaccharide component was more effective as a moisture barrier than similar films containing alternative polysaccharides (Table 3). HPMC was therefore used as the polysaccharide component in subsequent tests.

5

Figure 2 (lower curve) illustrates the reduced rate of water migration into the pastry base of a quiche in which the filling and the pastry base are separated by a film comprising collagen and HPMC, with a coating of acetylated monoglyceride.

10

(b) Pastry Crispness

The load/deformation characteristics of the pastry base measured on a tensile tester are shown in Figure 1. The three regions of the curve, A, B and C, are thought to correspond to the three layers of the cooked pastry, described above. The mean rupture load of the pastry decreased during storage, but the decrease was significantly less in quiches incorporating the film when compared with controls (Table 4).

15

20

(c) Taste Panel Assessments

The hedonic scores from a taste panel showed a clear improvement in "crispness" of the pastry in quiches with film (Table 5). The scores indicate consistently higher "brittleness" and lower "softness" for the film-containing samples.

25

30

(v) Detectability of the Film

A taste panel assessment showed that a non-neutralised collagen film was detectable in quiches - due to its texture and "bitter" taste. However, a collagen/Methocel/Dynacet film which was neutralised after extrusion using ammonia was not detected by a significant proportion of tasters (10/24 compared with an expected 8/24 in the BS 5929 Part 1

35

"triangle" test, 1980).

(vi) Effect of Film on Water Migration in Meat Pies

5 (a) Moisture Content

The moisture content of the base crust in control pies rose by 5.1% between 24 and 48h, whereas the moisture content of pies containing film rose only 0.7% (Table 6).  
10 The top crusts, however, showed a similar rise in water content in control and film-containing pies.

(b) Load/Deformation Properties

15 The rupture-load of the top and base crusts were measured 24 and 48h after cooking. The pies containing film showed a significantly lower rupture load than controls in the top crusts at both 24 and 48h, but a higher rupture load for the base crust (Table 7).

20

It will be appreciated that the present invention has been described above by way of example only, and that many variations are possible within the scope of the appendant claims.

TABLE 1

5 Water activity\* in quiche (without film) during storage

10	Time	Pastry	Filling
	90 minutes	0.943	0.978
15	24 hours	0.975	0.992
	48 hours	0.986	0.994
	120 hours	0.982	0.980

20

\* Decagon CX-1 water activity meter, 19.8 - 21.3°C

25

TABLE 2

30 Water uptake by pastry base of quiche  
with different film coatings

35	Film coating	Water uptake (%)
	None	33
40	Dynacet	20
	Beeswax	24
	Palm oil	27
45	Coconut oil	28
	Palm kernel oil	29

50

55

TABLE 3

Water uptake by pastry base of quiche  
with different polysaccharides

Polysaccharide component of film	Water uptake (%)
HPMC	22
Starch	31
Guar gum	32
Pectin	34
Control (no film)	28

TABLE 4

Force/deformation characteristics of  
quiche pastry during storage

Time	Rupture load	
	Control	Film
90 minutes	24.5 ± 9.6	20.0 ± 4.5
24 hours	13.5 ± 7.0	15.0 ± 4.9
48 hours	11.5 ± 2.3	15.3 ± 6.2*
120 hours	7.4 ± 1.6	15.0 ± 5.5*

\* indicates significant difference from control ( $p < 0.05$ )

TABLE 5Taste panel hedonic scores for quiches during storage

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Time	Softness*		Brittleness*	
	Control	Film	Control	Film
90 minutes	4.0	4.9	3.7	2.4
24 hours	2.8	3.5	4.4	4.0
48 hours	2.8	3.0	5.0	4.7
120 hours	2.2	2.1	5.8	6.3

\* the higher the score, the less acceptable the product

25

TABLE 6Moisture content (%) of meat filled pies during storage

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35

Time	Base crust		Top crust	
	Control	Film	Control	Film
24 hours	29.7	28.1	16.4	17.3
48 hours	34.8	28.8	19.2	21.6

40

TABLE 7Rupture loads for meat pie crusts during storage

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55

Time	Base crust		Top crust	
	Control	Film	Control	Film
24 h	5.2 ± 0.9	8.7 ± 1.3*	26.2 ± 11.0	13.8 ± 1.6*
48 h	6.6 ± 1.7	7.8 ± 1.3	26.3 ± 17.3	16.1 ± 6.3*

\* significantly different from control (p<0.05, n=6)

## CLAIMS

1. A film comprising an edible protein and an edible polysaccharide, said film having a coating of an edible hydrophobic material on at least a portion of a surface thereof.
2. A film according to claim 1 wherein said edible protein is a fibrous protein or a modified fibrous protein.
3. A film according to claim 2, wherein the fibrous protein is collagen.
4. A film according to any preceding claim, wherein the polysaccharide is selected from charged polysaccharides, gums and modified celluloses.
5. A film according to claim 4 wherein the polysaccharide is hydroxypropylmethylcellulose.
6. A film according to any preceding claim, wherein the hydrophobic material is an edible oil or wax.
7. A film according to claim 6 wherein the hydrophobic material is an esterified glyceride.
8. A film according to claim 7 wherein the esterified glyceride is acetylated monoglyceride.
9. A film according to any preceding claim wherein the film comprises from 3.5 to 60% protein, from 3.5 to 60% polysaccharide, and from 0 to 40% plasticiser, said percentages being by weight of the uncoated film.
10. A film according to any preceding claim wherein the hydrophobic material is present in an amount of from 10 to 50 g/m<sup>2</sup>.

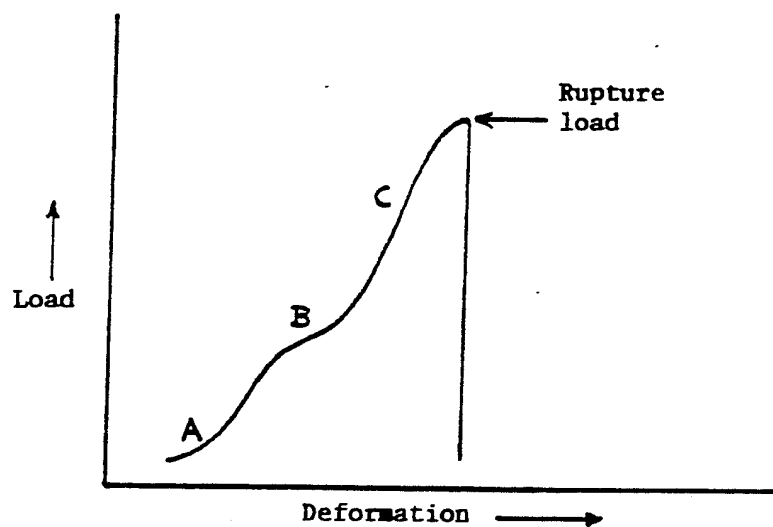
11. A food product comprising a domain of comparatively high moisture content and a domain of lower moisture content, said domains having a film according to any preceding claim disposed therebetween.

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12. A food product according to claim 11 wherein the domain of lower moisture content comprises pastry.

**SUBSTITUTE SHEET**

Fig 1: Penetrometer Load/Deformation Characteristics on Quiche Pastry Base

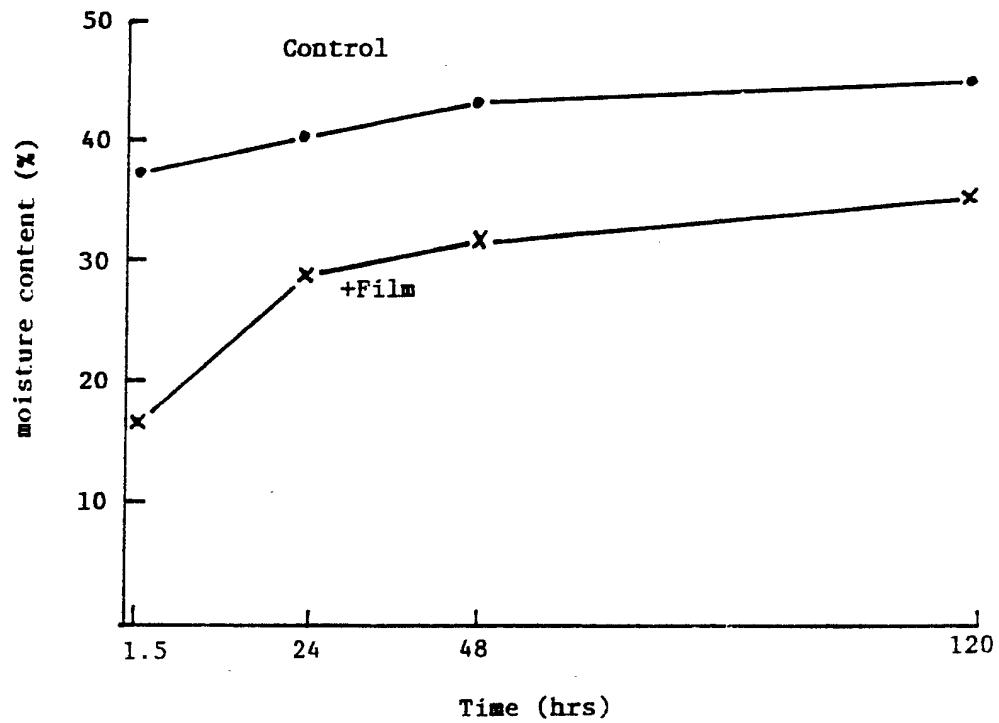


A, B and C indicate zones corresponding to the three visible layers of the baked pastry base from upper to lower, respectively (see text)



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Fig 2: The Effect of Barrier Film on the Moisture Content of Quiche Pastry



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 91/01244

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A23P1/08 ; A21D13/08

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System

Classification Symbols

Int.Cl. 5

A23P ; A21D

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	WO,A,8 600 501 (WISCONSIN ALUMNI RESEARCH FOUNDATION) 30 January 1986 see claims 1-16,42 see page 3, line 25 - page 6, line 10 see page 7, line 19 - page 8, line 6 see page 8, line 28 - page 9, line 20 ---	1-12
Y	WORLD PATENTS INDEX Derwent Publications Ltd., London, GB; AN 78-16712A(09) & JP,A,53 005 270 (SUMITOMO BAKELITE) 18 January 1978 see abstract --- -/--	1-12

<sup>10</sup> Special categories of cited documents :<sup>"A"</sup> document defining the general state of the art which is not  
considered to be of particular relevance<sup>"E"</sup> earlier document but published on or after the international  
filing date<sup>"L"</sup> document which may throw doubts on priority claim(s) or  
which is cited to establish the publication date of another  
citation or other special reason (as specified)<sup>"O"</sup> document referring to an oral disclosure, use, exhibition or  
other means<sup>"P"</sup> document published prior to the international filing date but  
later than the priority date claimed<sup>"T"</sup> later document published after the international filing date  
or priority date and not in conflict with the application but  
cited to understand the principle or theory underlying the  
invention<sup>"X"</sup> document of particular relevance; the claimed invention  
cannot be considered novel or cannot be considered to  
involve an inventive step<sup>"Y"</sup> document of particular relevance; the claimed invention  
cannot be considered to involve an inventive step when the  
document is combined with one or more other such docu-  
ments, such combination being obvious to a person skilled  
in the art.<sup>"&"</sup> document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

23 OCTOBER 1991

Date of Mailing of this International Search Report

07. 11. 91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

VUILLAMY V.M.L.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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Y	WORLD PATENTS INDEX Derwent Publications Ltd., London, GB; AN 72-43987T(27) & JP,B,47 023 384 (NITTA ZERACHIN) 1972 see abstract ---	1-12
Y	FR,A,2 097 896 (UNILEVER) 3 March 1972 see claims 1-3,5,7 see page 1, line 17 - page 2, line 36 ---	1-12
Y,P	EP,A,0 383 134 (NATURIN-WERK BECKER) 22 August 1990 see claims 1-6 see column 3, line 22 - line 39 ---	1-12

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. GB 9101244  
SA 49627**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 23/10/91

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		AU-A- 5107290	05-09-90
		WO-A- 9009105	23-08-90

**PUB-NO:** WO009201394A1  
**DOCUMENT-IDENTIFIER:** WO 9201394 A1  
**TITLE:** MOISTURE BARRIER FILM  
**PUBN-DATE:** February 6, 1992

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**PRIORITY-DATA:** GB09016340A (July 25, 1990)

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**EUR-CL (EPC):** A23L001/00 , A21D013/08 ,  
A23L001/00